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The excess of the energy supplied to the body over and above the external work done by the body is $q - w$. It follows from the *principle of conservation of energy* that the internal energy of the system must increase by $q - w$.

That is,

$$\Delta u = q - w$$

where Δu is the change in internal energy of the system.

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$$du = dq - dw$$

where dq is the differential increment of heat added to the system, dw the differential element of work done by the system, and du the differential increase in internal energy of the system.

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The change in internal energy du depends only on the initial and final states of the system, and is therefore independent of the manner by which the system is transferred between these two states. Such parameters are referred to as *functions of state*

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The volume of the substance is proportional to the distance from the base of the cylinder to the face of the piston, and can be represented on the horizontal axis of the graph shown in the following figure. The pressure of the substance in the cylinder can be represented on the vertical axis of this graph.

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The volume of the substance is proportional to the distance from the base of the cylinder to the face of the piston, and can be represented on the horizontal axis of the graph shown in the following figure. The pressure of the substance in the cylinder can be represented on the vertical axis of this graph.

Therefore, every state of the substance, corresponding to a given position of the piston, is represented by a point on this pressure-volume (p–V) diagram.

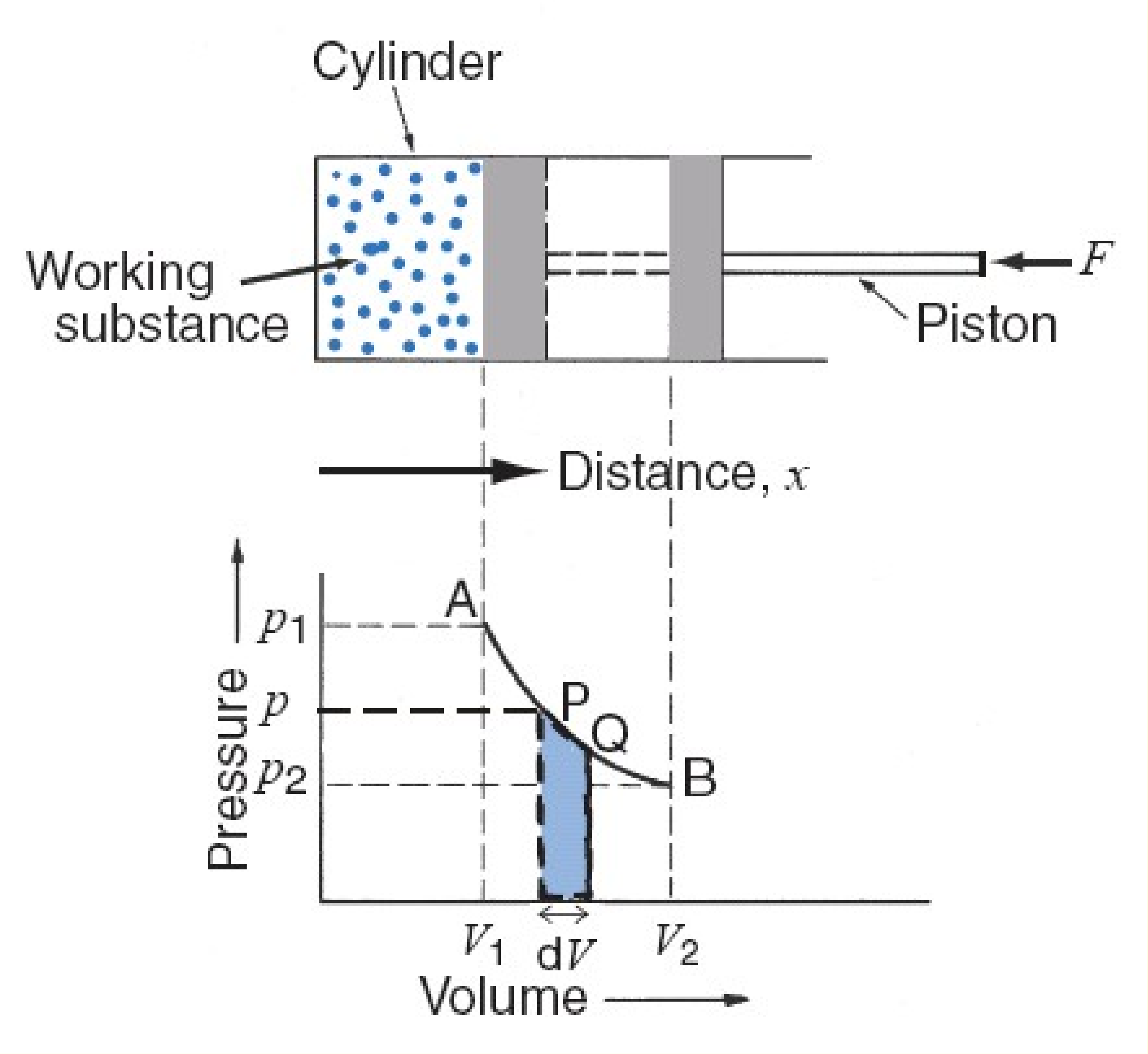

Figure 3.4: Representation of the state of a working substance in a cylinder on a p–V diagram.

If the piston moves outwards through an incremental distance dx, the work dW done by the substance in pushing the external force F through the distance dx is

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When the substance passes from state A with volume V_1 to state B with volume V_2, the work W done by the material is equal to the area under the curve AB. That is,

$$W = \int_{V_1}^{V_2} p\,dV$$

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If $V_2 > V_1$, then W is positive, indicating that the substance does work on its environment. If $V_2 < V_1$, then W is negative, which indicates that the environment does work on the substance.

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The p–V diagram is an example of a *thermodynamic diagram*, in which the physical state of a substance is represented by two thermodynamic variables. Such diagrams are very useful in meteorology; we will discuss other examples later, in particular, the *tephigram*.

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The thermodynamic equation may be written

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Using this with the equation above, we get

$$dq = du + p\,d\alpha$$

which is an alternative statement of the First Law of Thermodynamics.

Joule’s Law

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Joule's Law leads to an important conclusion concerning the internal energy of an ideal gas. If a gas neither does external work nor takes in or gives out heat, $dq = 0$ and $dw = 0$, so that, by the First Law of Thermodynamics, $du = 0$.

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According to Joule's law, under these conditions the temperature of the gas does not change, which implies that the kinetic energy of the molecules remains constant.

Therefore, since the total internal energy of the gas is constant, that part of the internal energy due to the potential energy must also remain unchanged, even though the volume of the gas changes.

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In this case, the internal energy of an ideal gas will depend only on its temperature:

$$u = u(T)$$

Specific Heats

Suppose a small quantity of heat dq is given to a unit mass of a material and, as a consequence, the temperature of the material increases from T to $T + dT$ without any changes in phase occurring within the material.

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But if the volume of the material is constant, the thermodynamic equation gives $dq = du$.

Again, $c_v = (dq/Dt)_V$. But V constant implies $dq = du$. Therefore

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For an ideal gas, Joule's law applies and therefore u depends only on temperature. Therefore, regardless of whether the volume of a gas changes, we may write

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Since u is a function of state, no matter how the material changes from state 1 to state 2, the change in its internal energy is

$$u_2 - u_1 = \int_{T_1}^{T_2} c_v\,dT$$

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In this case, some of the heat added to the material will have to be expended to do work as the system expands against the constant pressure of its environment.

Therefore, a larger quantity of heat must be added to the material to raise its temperature by a given amount than if the volume of the material were kept constant.

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For the case of an ideal gas, this inequality can be seen mathematically as follows. We write the thermodynamic equation as

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Using this in the equation above it, we obtain an alternative form of the First Law of Thermodynamics:

$$dq = c_p\,dT - \alpha\,dp\,.$$

The specific heats at constant volume and at constant pressure for dry air are 717 and $1004\,\mathbf{J\,K^{-1}kg^{-1}}$, respectively, and the difference between them is $287\,\mathbf{J\,K^{-1}kg^{-1}}$, which is the gas constant for dry air.

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Again,

$$c_v = 717 \qquad c_p = 1004 \qquad R = 287$$

(all in units $1004\,\mathbf{J\,K^{-1}kg^{-1}}$).

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Since the atmosphere is comprised primarily of diatomic gases ($\mathbf{N}_2$ and $\mathbf{O}_2$), we have

$$\gamma = \frac{c_p}{c_v} \approx \frac{7}{5} = 1.4\,, \qquad \kappa = \frac{R}{c_p} \approx \frac{2}{7} = 0.286\,.$$

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Moreover,

$$R \approx \frac{2}{7} \times 1000 \approx 286\,\mathbf{J\,K^{-1}kg^{-1}}$$

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Therefore, the finite quantity of heat Δq added is given by

$$\begin{aligned}\Delta q &= (u_2 - u_1) + p(\alpha_2 - \alpha_1) \\ &= (u_2 + p\alpha_2) - (u_1 + p\alpha_1)\end{aligned}$$

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where u_1 and u_2 are the initial and final internal energies for unit mass.

We define the *enthalpy* of a unit mass of the material by

$$h = u + p\alpha\,.$$

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From above it follows that, at constant pressure,

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Differentiating the defining equation, $h = u + p\alpha$, we obtain

$$\begin{aligned} dh &= du + d(p\alpha) \\ &= du + p\,d\alpha + \alpha\,dp \\ &= dq + \qquad\quad \alpha\,dp \end{aligned}$$

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Transferring terms to the other side, we get:

$$dq = dh - \alpha\,dp\,.$$

This is another form of the First Law of Thermodynamics.

Repeating,

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$$dq = c_p\, dT - \alpha\, dp\,.$$

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or, in integrated form,

$$h = c_p T$$

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In view of this, h is sometimes called the *heat at constant pressure*, because it corresponds to the heat given to a material to raise its temperature from 0 to T Kelvins at constant pressure.

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Hence, if the material is a parcel of air with a fixed mass that is moving about in an hydrostatic atmosphere, the quantity

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For *adiabatic changes*, the dry static energy is constant.

Exercises: